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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
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Additional inventors are being named on the 1 separately numbered sheets attached hereto**TITLE OF THE INVENTION (500 characters max)**

METAL-MEDIATED AERATION FOR WATER AND WASTEWATER PURIFICATION

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METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.	FILING FEE Amount (\$)
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<input checked="" type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: <u>50-0951</u>	80.00
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

<input type="checkbox"/> No.	
<input checked="" type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: <u>U.S. Dept. of Energy</u> <u>Grant No. DE-AC26-01NT41302</u>	

[Page 1 of 2]

Respectfully submitted,

Date October 29, 2003

SIGNATURE

REGISTRATION NO. 46,803TYPED or PRINTED NAME Neil R. Jetter

(if appropriate)

TELEPHONE 561-653-5000Docket Number: 7320-20**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

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Docket Number 7320-20

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METAL MEDIATED AERATION FOR WATER
AND WASTEWATER PURIFICATION

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(UM Disclosure No. UM04-02)

AKERMAN SENTERFITT DOCKET No.: 7320-20

METAL MEDIATED AERATION FOR WATER
AND WASTEWATER PURIFICATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not applicable.

STATEMENT REGARDING FEDERALLY SPONSORED
RESEARCH OR DEVELOPMENT

[0002] The United States Government has certain rights to this invention pursuant to U.S. Department of Energy Grant No. DE-AC26-01NT41302.

FIELD OF THE INVENTION

[0003] The invention relates to water and soil purification, more particularly to purification systems and methods based on metal-mediated aeration.

BACKGROUND

[0004] Over six million new chemicals are estimated to have been introduced to the environment by humanity, including 60-95 thousand produced commercially, and another thousand added each year. Many of these chemicals are accumulating in waters and living tissues. While long-term environmental and health impacts of many of these chemicals are not well understood, some of these compounds are known to cause estrogenic or carcinogenic effects in humans and animals at concentrations found in certain natural waters. Moreover, recent studies have indicated the universal occurrence of industrial and agricultural chemicals in human blood samples.

[0005] Existing chemical processes for oxidizing organics and disinfecting water and wastewater generally use chemical, thermal, or radiant energy as input. Chlorination is a

common water purification method. However, chlorination imparts emerging chlorinated contaminants. Membrane filtration and adsorption is another common water purification method. However, applications for membrane filtration and adsorption are generally limited because contaminants are transferred to another phase, and thus not destroyed. Advanced oxidation processes are generally capable of efficiently oxidizing organics in water, and include electron beam treatment, Fenton processes (using hydrogen peroxide), UV/titanium dioxide, UV/ozone processes, and simple ozonation. However, these advanced oxidation processes do not effectively remove inorganic contaminants. Therefore, economical methods for effectively decomposing and removing emerging contaminants including both organic and inorganic contaminants from water, wastewater and solid media, such as sediment, are needed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] A fuller understanding of the present invention and the features and benefits thereof will be accomplished upon review of the following detailed description together with the accompanying drawings, in which:

[0007] Figure 1 shows one design of a metal mediated aeration-based water treatment system, according to an embodiment of the invention.

[0008] Figure 2 is a schematic of a system for remediation of dredged sediment, according to another embodiment of the invention.

[0009] Figure 3 is a schematic of a system according to an embodiment of the invention for iron-mediated aeration/vertical circulation process for removing mixtures of cationic and anionic metals, radionuclides, and organics, from groundwater and soils.

[00010] Figure 4 is a schematic diagram of a bench scale non-energized fixed bed reactor used for certain experiments performed according to the invention.

[00011] Figure 5(a) provides data showing EDTA decomposition versus non-energized treatment time with and without aeration (oxygen), while Figure 5(b) provides data shows EDTA decomposition versus non-energized treatment time with and without ambient light, according to an embodiment of the invention.

[00012] Figure 6 shows concentrations of a variety of metallic cations and anions initially (influent), and after 25 hours of aeration with filtration (effluent), according to an embodiment of the invention.

[00013] Figure 7(a) shows initial and final metal concentrations of metals following 25 hours treatment in a non-energized reaction according to the invention, for simultaneous treatment of mixtures of nickel, cadmium, lead and mercury, while Figure 7(b) shows system performance for simultaneous treatment of mixtures of oxides of arsenic, vanadium and chromium.

[00014] Figure 8 shows glyoxylic acid production versus time using a non-energized mediated aeration process according to an embodiment of the invention.

[00015] Figure 9(a) shows removal efficiency in energized reactors including continuous ultrasonic energy, with and without iron, showing the effect of aeration and deaeration, while FIG. 9(b) shows removal efficiency using continuous ultraviolet energy, compared with same reactor operated without energy, according to the invention, according to an embodiment of the invention.

[00016] Figure 10 shows cadmium removal vs. aeration/illumination time in a UV-assisted reactor described as compared to operation of the same reactor without UV illumination, according to an embodiment of the invention.

[00017] Figure 11 shows EDTA removal versus time of catalytic aeration, with and without application of pulsed ultrasonic energy (60 seconds on, 60 seconds off), 94-95 W/cm², in identical reactors, according to an embodiment of the invention.

[00018] Figure 12 shows cadmium removal versus time of catalytic aeration, with and without application of pulsed ultrasonic energy (60 seconds on, 60 seconds off), 94-955 W/cm², in identical reactors, according to an embodiment of the invention.

[00019] Figure 13 shows the removal of 17 β -estradiol and di-n-butyl phthalate from simulated natural water at pH ~7 with 24 hours aeration, using the invention.

[00020] Figure 14 shows disinfection kinetics for the invention applied to coliform bacteria, according to an embodiment of the invention.

DETAILED DESCRIPTION

[00021] A water treatment method includes the steps of providing a solid fluid permeable metal arrangement, such as a volume of Fe filings or steel wool, and contacting influent water including at least one contaminant with the metal in the presence of an oxygen comprising gas flow. The oxygen comprising gas is generally air, but the invention is in no way limited to air. As used herein, the phrase "water treatment" is meant to be interpreted broadly to include waste water, drinking water and other water forms having one or more contaminants which can benefit from remediation processing.

[00022] The metal can be a transition metal other than Fe, or certain non-transition metals, such as Al. The metal preferably provides a high surface area to volume ratio, such as is available from porous or solid metal granules, micro size or nanosize particles, or metal fibers. A resulting outlet flow following the contacting step provides a reduction in a concentration of the contaminant which has been present in the influent and/or precipitation, co-precipitation or reduction to metal form of at least a portion of the influent contaminant with the metal to form a metal sludge (e.g. an Fe sludge). The method can include one or more separating steps such as sedimentation and/or filtration of the metal sludge from the outlet flow. In a preferred embodiment of the invention, the metal comprises Fe, as Fe is non-toxic, and Fe(III) residuals, such as in the form of an Fe sludge, produced by the inventive process are generally filterable.

[00023] Figure 1 shows an exemplary metal mediated aeration-based water treatment system 100, according to an embodiment of the invention. The system 100 includes a fluidized bed reactor 110 and a sedimentation filter 140. Although a fluidized bed reactor 110 is shown in Figure 1, a standard fixed reactor is generally suitable for use with the invention.

[00024] The solid fluid permeable metal arrangement used in reactor 110 is a volume of Fe filings 115. Reactor includes an inlet 116 for receiving influent water including at least one contaminant 120 and another inlet 117 for receiving air 125. Contaminants can include organic contaminants, inorganic contaminants, as well as microbials, such as protozoa and viruses. Organic contaminants are generally oxidized, inorganics are generally precipitated together with Fe to form a sludge, while microbials are generally deactivated by reactor 110.

[00025] Influent water including contaminant(s) is contacted by the Fe filings 115 in the presence of oxygen provided by air 125. Air 125 is preferably provided by a continuous flow source. Although pH adjustment is generally not required, in certain situation it may be desirable to either raise or lower the pH in reactor 110 to increase the efficiency of the remediation process. In this embodiment, a further step of neutralization can be performed prior to releasing effluent 150.

[00026] A resulting outlet flow 130 from reactor 110 following the contacting step provides a reduction in a concentration of the contaminant in the influent and/or precipitation or co-precipitation of at least a portion of the influent contaminant with the metal to form a metal sludge, here an Fe sludge. Part of the outlet flow 130 is recirculated for additional treatment in reactor 110 through fluid connection 135, to achieve the desired mean residence time in the reactor. Remaining flow is directed to the sedimentation basin 140 for separation of the Fe sludge to provide treated effluent 150.

[00027] A sedimentation basin is only one possible embodiment of a separation device for separating the Fe sludge 145 from treated effluent 150. For example, sand filters or membrane filters can be used, with or without pretreatment by sedimentation. Although System 100

includes a separation device embodied as a sedimentation basin 140, in some applications, sedimentation basin 140 will not be needed.

[00028] Figure 2 is a schematic of a system 200 for remediation of dredged sediment, according to an embodiment of the invention. System 200 implements a 2-phase remediation process comprising an extraction phase 230 and an oxidation/co-precipitation phase 260. As shown in Figure 2, sediment 210 is flushed in an upflow mode to remove organics and metals. If needed, as shown in FIG. 2 EDTA or another other suitable chelating agent is added to extract any cationic contaminant metals in the sediment 210 into the aqueous phase. If levels of insoluble organics are significant, a measured amount of surfactant is added for organic extraction.

[00029] The extractant from the extraction phase 220 is then subjected to an oxygen comprising gas (e.g. aerated) in the presence of a natural, mineral “catalyst” in the oxidation/precipitation/co-precipitation phase of the remediation process. The term “catalyst” is used here broadly to refer to an auxiliary reactant that, although it is consumed in the reaction, accelerates the primary reaction. A mineral “catalyst” generally is defined herein as a metallic specie, such as Fe in the form of iron filing or steel wool, or high surface area aluminum particles. The mineral-mediated aeration in phase 2 oxidizes organics, including contaminants, EDTA, and surfactants, and co-precipitates cationic metals and anionic metal oxides in the water. For example, EDTA, estrogen, and n-dibutylphthalate have been oxidized, and strontium, cadmium, lead, mercury, nickel, arsenate, arsenite, vanadate, and chromate have been found to be removed, presumably by co-precipitation, in experiments performed.

[00030] Outlet flow 265 from the oxidation/co-precipitation process is directed to sedimentation filter 270. Sedimentation filter separates clean water 275 from sludge and trace

metals 280. Clean water 275 can be output by system 200, or filtered by filter 285 and then sent for one or more additional cycles of remediation processing.

[00031] Figure 3 is a schematic of a system 300 for iron-mediated aeration/vertical circulation process for removing mixtures of cationic and anionic metals and radionuclides, and organics, from groundwater and soils via a well 310. Conduit 320 provides air to the base of well 310. Chelator/surfactant 330 and steel wool/Fe 340 are provided by system 300.

[00032] Using systems according to the invention, organics, including bio-toxics, in both water and wastewater can be oxidized at rates of at least that of conventional activated sludge treatment. In particular, organics such as estrogen, alkylphenolics (e.g., 4-nonylphenol), biphenolics (e.g., bisphenol A), and other alcohol compounds can be oxidized, along with compounds having carboxylic groups, nitrogenous electron pairs, covalent or aromatic bonding, or electron-rich centers with coordination to oxygen centers. Treatable organics also include di-n-butyl phthalate, NDMA, pesticides, and pharmaceuticals. Because the principal oxidants are thought to be hydroxyl radical and/or ferryl/perferryl ions, it is likely that oxidation of organics will be indiscriminant. Byproducts produced by the metal mediated aerobic oxidation process will generally include CO₂ and, depending on time of treatment, relatively simple, biodegradable organics.

[00033] The inventive process also removes inorganics, such as by transition metal-mediated aeration. For example, treatable inorganics include arsenite, arsenate, mercury, chromate, nickel, lead, cadmium, vanadate, strontium, nitrate, phosphate, perchlorate, and radionuclides (See Figure 6 and accompanying description).

[00034] Further, the process can be used for the disinfection of water, including cellular organisms (e.g. protozoans) and RNA (e.g. viruses). Thus systems according to the invention

can eliminate the formation of chlorinated byproducts such as nitroso-dimethylamine (NDMA, a potent carcinogen) generated by conventional chlorination processing. Perchlorate may also be removed using the invention based on preliminary results obtained for oxidic anions.

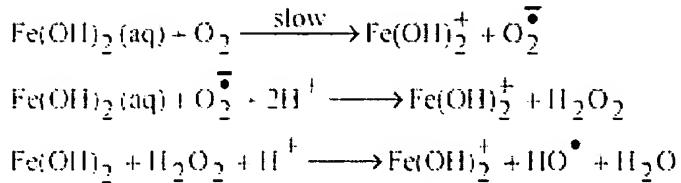
[00035] Although described primarily for elimination of organics and removal of inorganics from water or wastewater, as shown by system 200 relative to FIG. 2, the invention can also generally be applied to solid media. For example, through use of a suitable chelating extraction agent, such as EDTA, solid media including soil and sediment (e.g. dredged sediment). The chelating agent upon contact with a variety of inorganics forms a fluid including complexed contaminants which can be treated using metal mediated aeration according to the invention. EDTA extraction is particularly effective for certain cationic metals.

[00036] Turning now to a comparison of the invention to related art, the superoxide anion radical ($O_2^{\bullet-}$) is known to react with hydrogen peroxide (H_2O_2) to produce O_2 , OH^- , and hydroxyl radical (HO^{\bullet}). However, this reaction is known to proceed at an insignificant rate. In the presence of Fe(II), the Fenton reaction occurs. In the Fenton reaction, Fe(II) is oxidized to Fe(III) by molecular oxygen, superoxide, and peroxide and results in the formation of superoxide, peroxide, and hydroxyl radical, respectively. The hydroxyl radical (HO^{\bullet}) can in turn oxidize Fe(II) to Fe(III). Thus, Fenton systems produce H_2O_2 and HO^{\bullet} . Both are powerful oxidants, with oxidation power relative to chlorine of about 1.31 for H_2O_2 and 2.06 for hydroxyl radical. The iron-catalyzed formation of HO^{\bullet} from superoxide is favored at low pH (<5.5), and when at least one iron coordination site is open or occupied by a readily dissociable ligand such as water.

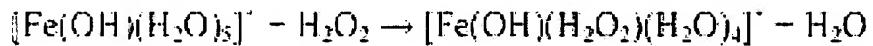
[00037] In the reactions discussed above, H_2O_2 provides the requisite chemical energy for oxidation. In contrast, the invention can proceed with a non-energized, metal (e.g. Fe)-mediated

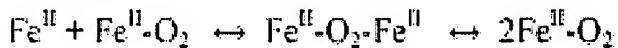
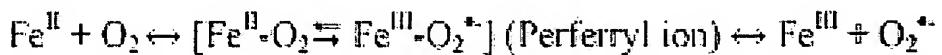
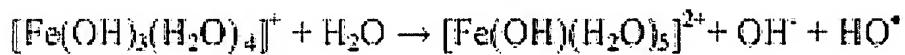
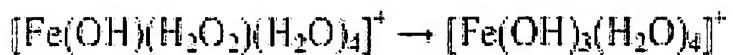
aeration process to oxidize organic pollutants and co-precipitate metals, inactivate coliform, *E. coli*, and other bacteria in water and wastewater. In one embodiment of the invention, the water or wastewater is continuously aerated in the presence of a volume of solid fluid permeable metallic iron. The non-energized process has been found to be not strictly catalytic, because oxidation is inhibited or stopped when the metallic Fe is removed. However, metals such as Fe greatly accelerate the oxidation of organics by molecular oxygen, during aeration.

[00038] Although not required to practice the invention, Applicants provide the following proposed mechanism that they do not seek to be bound by. A Fenton-like sequence, at neutral pH, can be driven by iron corrosion and aeration. That is, Fe(0) is continuously oxidized to Fe(II) and further to sparingly soluble Fe(III). Fortunately, $\text{Fe(OH)}_2(aq)$ is the thermodynamically-favored Fe(II) species, because this species has a rate constant for oxidation with molecular oxygen to produce superoxide radical that is five and twelve orders of magnitude higher than those of Fe^{2+} and FeOH^+ , respectively. Thus, superoxide radical may be produced rapidly enough in this rate-limiting step to drive the production of hydroxyl radical and/or ferryl species, as follows:



[00039] Hydroxyl radicals and hydrogen peroxide thus generated may produce ferryl/perferryl according to the following equations below:





[00040] Hydroxyl radical and ferryl moieties not scavenged by ferrous hydroxide or bicarbonate can indiscriminately oxidize organic contaminants. Assuming this mechanism, reactions occur at the Fe(II) interface between the metal and the oxy/hydroxy Fe(III) precipitate. Support for this mechanism are published results reporting negligible solution-phase oxidation in a Fenton system. However, in other types of advanced oxidation processes involving particulate catalysts, the catalyst with the largest surface area is not always the most active. If the process is indeed interfacial, then mass transfer characteristics of reactants, intermediates, and products to, and away from, the interfacial reaction zone will determine rates of organic oxidation and Fe(III) precipitation.

[00041] Thus, Fe(0) is believed to produce Fe(II), which may sequentially react with (a) O₂ to form superoxide, and (b) superoxide to form hydrogen peroxide. Hydrogen peroxide may then react with further Fe(II) to form hydroxyl radicals and/or Fe(IV), and higher valence Fe species. The hydroxyl radical is a powerful and indiscriminate oxidant, and ferryl and perferryl ions may have reactivities approaching that level. Furthermore, it has been found that cationic metals and anionic metal oxides (e.g. strontium, cadmium, lead, mercury, nickel, arsenate, arsenite, vanadate, and chromate) are removable from the water, presumably by co-precipitation, precipitation, or reduction to the metallic form.

[00042] It is believed that the principal oxidizing species generated are hydroxyl radicals and ferryl/perferryl ions generated at the Fe(II) interface. Thus, oxidation rates can be enhanced and sludge generation diminished through control of iron surface area, aeration rate, mixing energy, and reactor design. Reaction rates will generally be accelerated and sludge reduced by maximizing mass transfer and surface area, while retaining metallic iron (Fe^0) in the aeration zone, for example through the use of a fluidized bed reactor.

[00043] Mixing energy can be controlled using a plurality of process parameters. For example, mixing energy can be changed by changing the oxygen comprising gas flow, the water flow, or the speed of the mixing structure, such as a mixing propeller.

Another possible removal mechanism for metals and radionuclides is plating out of the metals and radionuclides on the metal catalyst, such as Fe. Most cationic metals other than sodium, aluminum, magnesium, and zinc can be reduced (e.g. Cd^{++} to Cd metal) by Fe metal which would be oxidized to Fe^{++} . In the aerated process where the iron surface is covered with hydroxide precipitate, particularly at low pH where the hydroxide sludge generally does not form, this mechanism can become significant along with co-precipitation and precipitation as possible removal mechanisms.

[00044] A preferred embodiment for practicing the invention is using a fluidized bed reactor, along with associated sedimentation and filtration, such as shown by system 100 in FIG. 1. Since unlike Fe(III) , $\text{Fe}(0)$ is paramagnetic, a fluidized bed reactor can include a magnetic field source so that magnetic separation can be used to retain metallic iron at the reaction interface, while maximizing mass transfer of Fe(III) away, and bulk solution to, the interface. However, it is believed that physical separation by straining and flow control will generally provide

equivalent separation with less complexity and expenditure of energy as compared to a magnetically fluidized bed reactor.

[00045] Although not required, reaction kinetics can be accelerated further by adding an externally supplied energy source. For example, as shown in the Examples, ultraviolet and ultrasonic energy have been demonstrated to improve process efficiency in tests performed. Ultraviolet energy can reduce sludge generation by reducing Fe^{+3} to Fe^{+2} . In addition, electromagnetic energy other than UV, such as RF which can be useful for heating water, can be used to increase reaction kinetics.

[00046] The invention is expected to have a wide range of applications since it effectively destroys organic contaminants in water and wastewater by simple aeration in the presence of iron, and removes metals, radionuclides, and other inorganics from water and wastewater by producing an iron sludge. Applications are expected to include water and wastewater utilities, particularly in light of recent and potential new regulation of disinfection byproducts, and recent regulation of arsenic in drinking water, and potential regulation of endocrine disrupting compounds (EDCs) in wastewater. The invention can also be applied to industrial wastewater treatment, such as for textiles, pulp and paper. The invention can also be applied to water treatment in developing countries, including addressing arsenic poisoning and cholera epidemics. Residential point-of-use drinking water systems can also be based on the invention. In addition, as noted above, through use of chelating agents the invention can also be used to treat solid media, such as soils and dredged sediment.

EXAMPLES

[00047] It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application. The invention can take other specific forms without departing from the spirit or essential attributes thereof.

[00048] In preliminary laboratory tests, water-metal-EDTA solutions were continuously aerated and circulated through steel wool for 24 hours, using the bench scale non-energized fixed bed reactor shown in Figure 4. Figure 5(a) shows EDTA decomposition versus non-energized treatment time with and without oxygen, while Figure 5(b) shows EDTA decomposition versus non-energized treatment time with and without ambient light. Samples contained 0.89 mM Cd²⁺ in simulated “natural” water (0.5 mM CaCl₂ and 3.28 mM NaHCO₃ (200 mg/L HCO⁻) adjusted to pH 7.5-7.6 with concentrated HCl) and 1.78 mM (516 mg/L) of EDTA⁴⁻. Three replicate samples were circulated in the reactor with aeration for 2 hr, 5 hr, 8hr, 16 hr, and 25 hr intervals.

[00049] Figure 6 shows concentrations of a variety of metallic cations and anions initially, and after 25 hours aeration with filtration. Results shown are the mean of three replicate samples with +1 standard deviation shown. 10-20 mg/L of each metal was added to two times the stoichiometric amount of EDTA for complexation, in simulated natural water, and tested using procedure described above relative to FIGs. 5(a) and 5(b).

[00050] Figure 7(a) shows initial and final metal concentrations of metals following 25 hours treatment in a non-energized reaction according to the invention, for simultaneous treatment of mixtures of nickel, cadmium, lead and mercury, while Figure 7(b) shows system performance for simultaneous treatment of mixtures oxides of arsenic, vanadium and chromium. 10 mg/L of each

cationic metal was added as Hg (from HgCl_2), Ni (from $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), Pb (from $\text{Pb}(\text{NO}_3)_2$), and Cd (from CdCl_2) with two times the stoichiometric amount of EDTA for complexation, in synthetic “natural” water, and tested using procedure described relative to Figures 5(a) and 5(b). Approximately 10-20 mg/L of each anionic metal was added as K_2CrO_4 , NaO_3V , Na_2HAsO_4 , and NaAsO_2 without EDTA, in synthetic “natural” water. Results shown are the mean of four replicate samples ± 1 standard deviation.

[00051] Preliminary analyses of EDTA decomposition byproducts in initial process tests described here indicated that the EDTA may have been largely mineralized to CO_2 after 25 hours. Other byproducts of EDTA decomposition were simple, naturally occurring, rapidly biodegradable organic byproducts that may be removed with minor process adjustment. Specifically, as shown in FIG. 8, after 25 hours of treatment, 0.21 mM glyoxylic acid, 0.15 formaldehyde, and 0.02 mM EDTA from the concentration disclosed relative to FIGs. 5(a) and 5(b) remained, accounting for 3%, 2%, and 2% of the original EDTA mass, respectively. The percentages for glyoxylic acid and formaldehyde noted assume that each EDTA molecule is decomposed to four glyoxylic acid or formaldehyde molecules. If significant ED3A or related compound remains after 24 hours, the percentages listed could be up to four times as high, though this is not considered likely based on qualitative analyses of large molecular weight byproducts. Natural formaldehyde is present in raw food, and it is a normal metabolite in the human body. Formaldehyde is permitted as an indirect food additive and is used in mouthwash, toothpaste, and foot powder. Formaldehyde has a half-life of 2-20 days in water.

[00052] Minor amounts of iminodiacetic acid and ED3A (an impurity in EDTA) were detected, both having no known health effects. Some samples contained traces of nitrilotriacetic acid, readily biodegradable and not regulated. Simple organic acids (e.g., acetic, oxalic, formic,

malonic) were expected, but not found, in high-pressure liquid chromatographic (HPLC) results, suggesting mineralization or co-precipitation. However, chromatographic parameters can be refined further to target such potential byproducts. Nitrate has not yet been detected in the effluent, though the two principal nitrate methods used to date may not have the sensitivity required and further confirmation is needed. This result, taken together with literature information on nitrate removal mechanisms, suggests co-precipitation of nitrate.

[00053] Tests have also been conducted with ultrasonic and ultraviolet-energized, iron-mediated aeration reactors. Because the reactor designs were modified somewhat to accommodate the additional equipment, non-energized tests were repeated in the modified reactors for comparison with energized results. Non-energized removals in the modified laboratory reactors were somewhat lower than in the original non-energized reactors, presumably due to altered mass transfer characteristics.

[00054] Figure 9(a) shows removal efficiency in energized reactors including continuous ultrasonic energy, with and without iron, showing the effect of aeration and deaeration, while FIG. 9(b) shows removal efficiency using continuous ultraviolet energy, compared with same reactor operated without energy. Conditions were otherwise the same as described relative to FIGs. 5(a) and 5(b). The ultrasonic energy was 94-98 W/cm² ultrasonic energy, while the ultraviolet energy was provided by a 450-Watt medium pressure, quartz mercury vapor UV lamp. As shown in FIGs. 9(a) and 9(b), removal rates were doubled using ultraviolet energy, and quadrupled using continuous ultrasonic energy as compared to the results shown in FIGs. 5(a) and 5(b), which did not include an external energy source. Removal using pulsed ultrasonic energy (not shown here) was up to twice as high as in non-energized tests. No measurable

differences in the byproducts of the UV and US-energized processes were found as compared with the non-energized process.

[00055] Figure 10 shows cadmium removal vs. aeration/illumination time in the UV-assisted reactor described above, as compared to operation of the same reactor without UV illumination. UV illumination can be seen to significantly increase cadmium removal.

[00056] Figure 11 shows EDTA removal versus time of catalytic aeration, with and without application of pulsed ultrasonic energy (60 seconds on, 60 seconds off), 94-95 W/cm², in identical reactors. Ultrasonic energy can be seen to significantly increase the removal rate of EDTA.

[00057] Figure 12 shows cadmium removal versus time of catalytic aeration, with and without application of pulsed ultrasonic energy (60 seconds on, 60 seconds off), 94-955 W/cm², in identical reactors. Ultrasonic energy can be seen to significantly increase the removal rate of EDTA.

[00058] Figure 13 shows removal of 17- β estradiol and di-n-butyl phthalate from simulated natural water at pH ~7 with 24 hours aeration using the invention. The test procedure as described relative to FIGs. 5(a) and 5(b) were used, with analysis by LC-MS. Analysis of phthalate was in terms of phthalate ion, and no other significant phthalate species were observed.

[00059] The disinfection kinetics of the inventive process was studied. As shown in Figure 13, three logs removal of total coliform bacteria were achieved in one hour, a rate of disinfection equivalent to a total residual of 0.7 mg/L chlorine in secondary effluent. This rate can be enhanced significantly, for example in a fluidized bed reactor.

[00060] The goal in the experiments summarized herein was to maximize oxidation without regard for iron sludge production. Total iron concentrations obtained after acidification of the unfiltered solution following aeration were on the order of 800-2500 mg/L after 8 hours, one to two orders of magnitude higher than in conventional coagulation systems. However, those iron concentrations likely included broken steel wool particles that will not be present in a continuous-flow, optimized process. Generation of one mole of hydroxyl radical and three moles of Fe(III) per mole of organic in secondary effluent, assuming a number-average molecular weight for organics in secondary effluent of 1242 Daltons, would require generation of about 14 mg/L $\text{Fe}_2\text{O}_3/\text{L}$ secondary effluent. Theoretical minimum sludge mass would be lower still in water treatment applications. As noted earlier, if needed to reduce sludge or accelerate oxidation, ultraviolet energy can be used to convert Fe(III) back to Fe(II), making the process catalytic. However, test results have indicated that the non-energized process may be preferred in a variety of applications due to operational simplicity, efficiency, and stability.

[00061] It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application. The invention can take other specific forms without departing from the spirit or essential attributes thereof.

ABSTRACT

A water treatment method includes the steps of providing a solid fluid permeable metal arrangement, such as a volume of Fe filings or steel wool, and contacting influent water including at least one contaminant with the metal in the presence of an oxygen comprising gas flow. A resulting outlet flow following the contacting step provides a reduction in a concentration of the contaminant in the influent and/or precipitation, co-precipitation or reduction to metal form of at least a portion of the contaminant with the metal to form a metal sludge. The method can include a separating step including sedimentation or filtration of the metal sludge from the outlet flow.

100

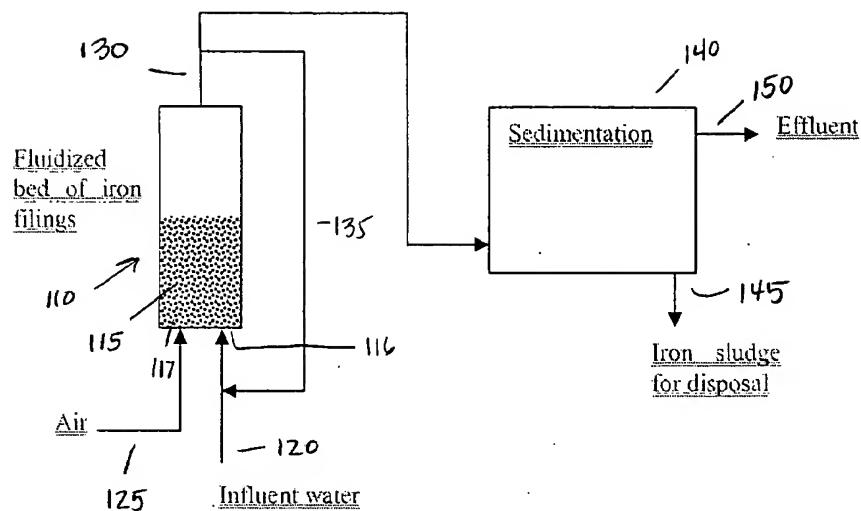


FIG. 1

200

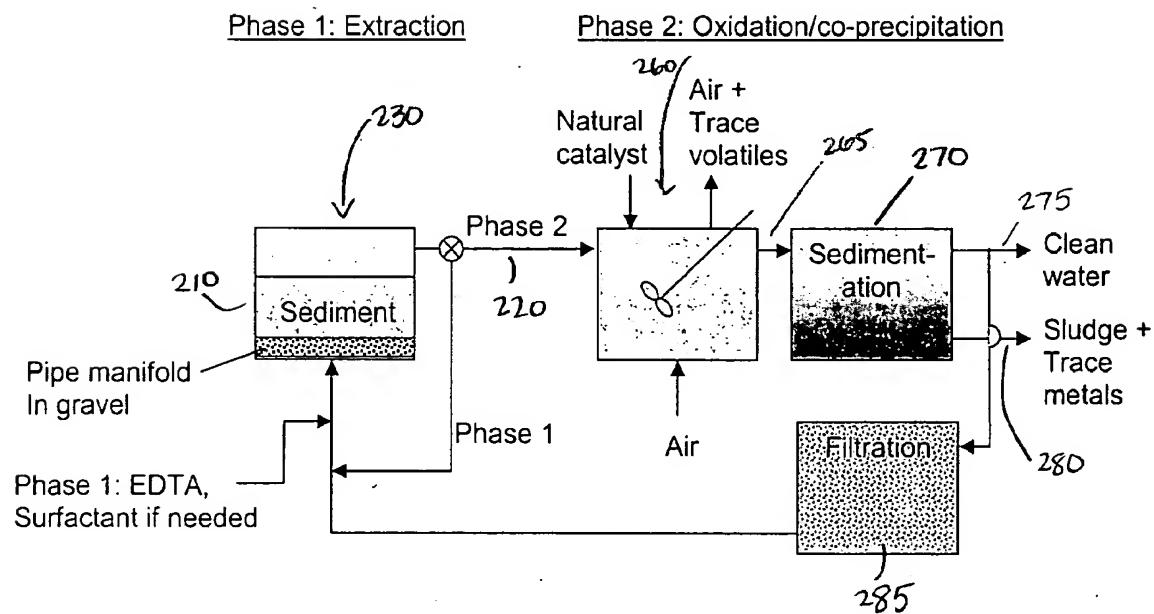


FIG. 2

300

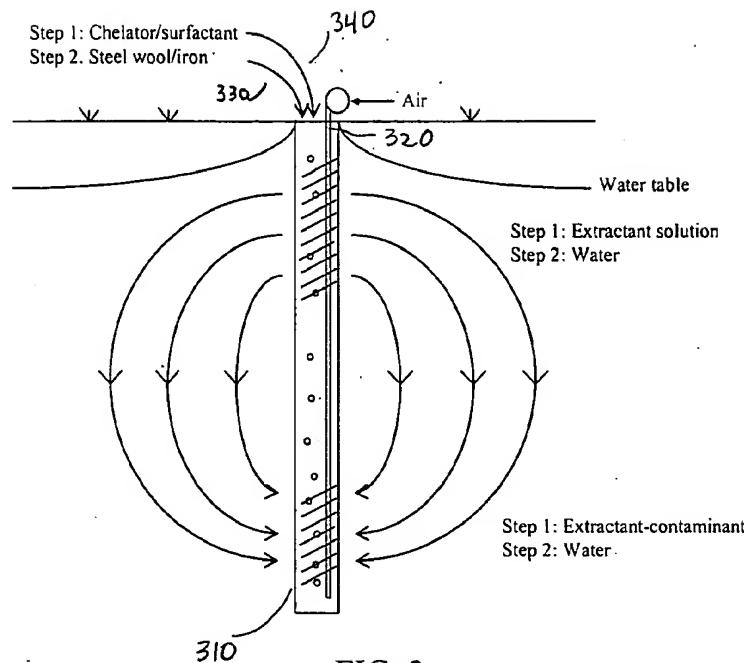


FIG. 3

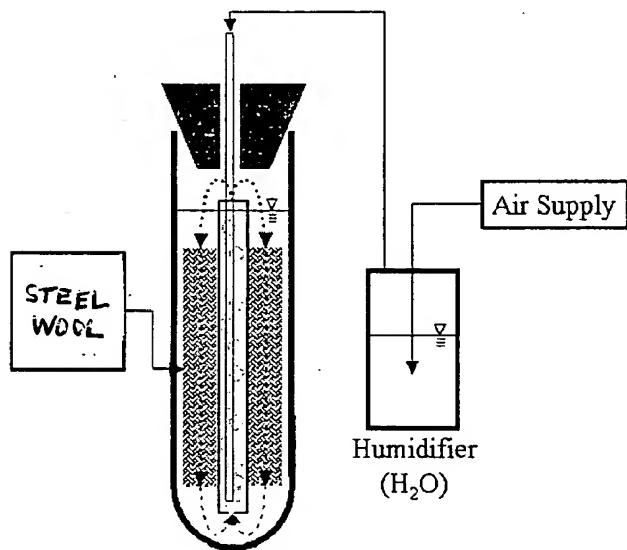


FIG. 4

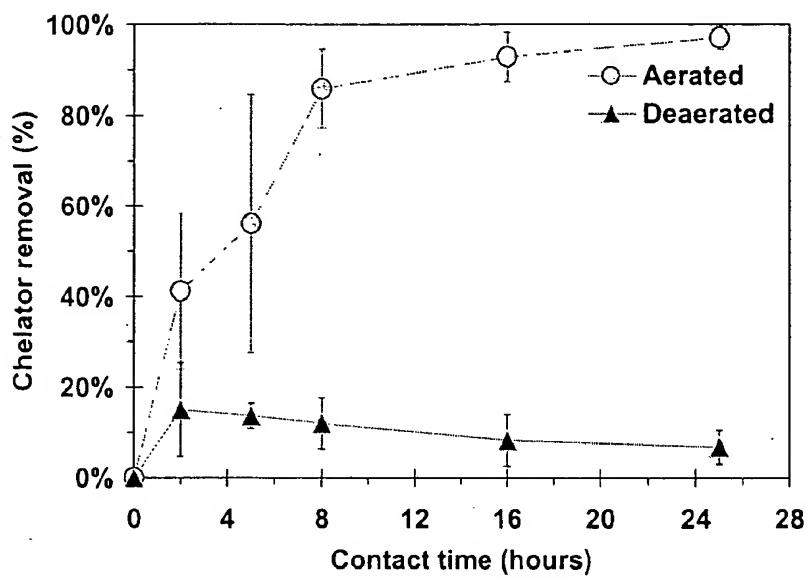


FIG. 5a

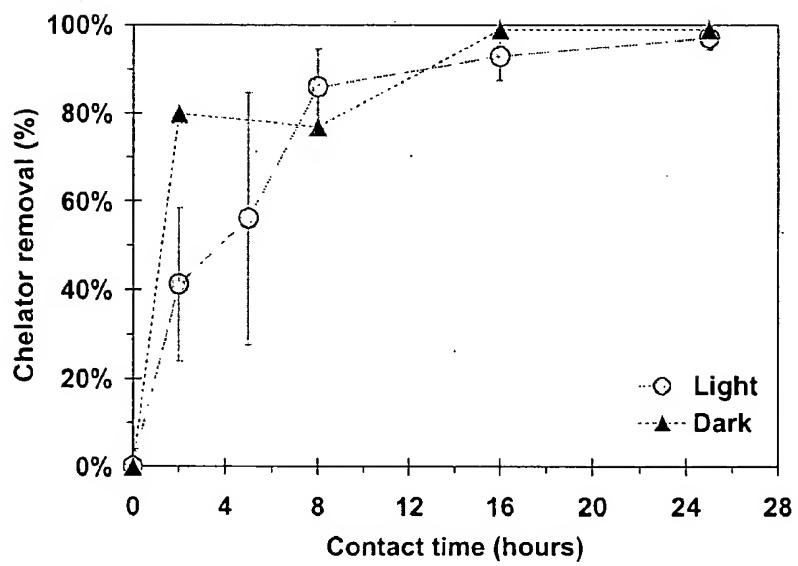


FIG. 5b

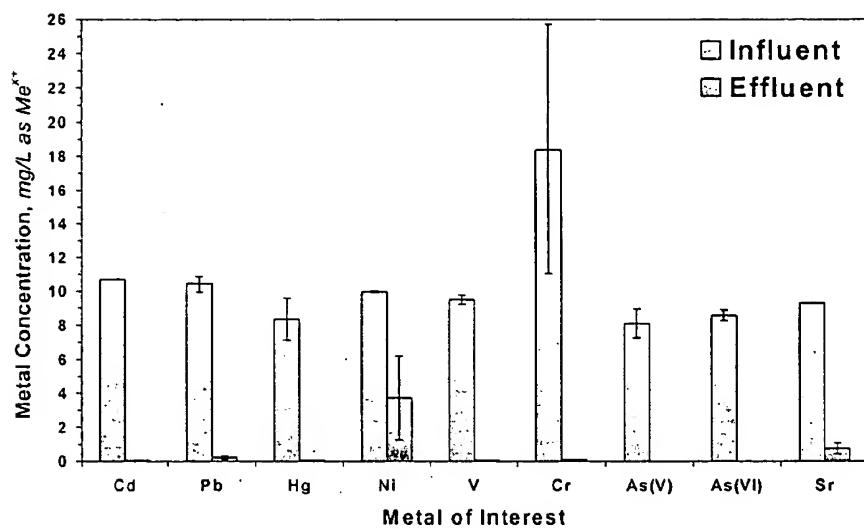


FIG. 6

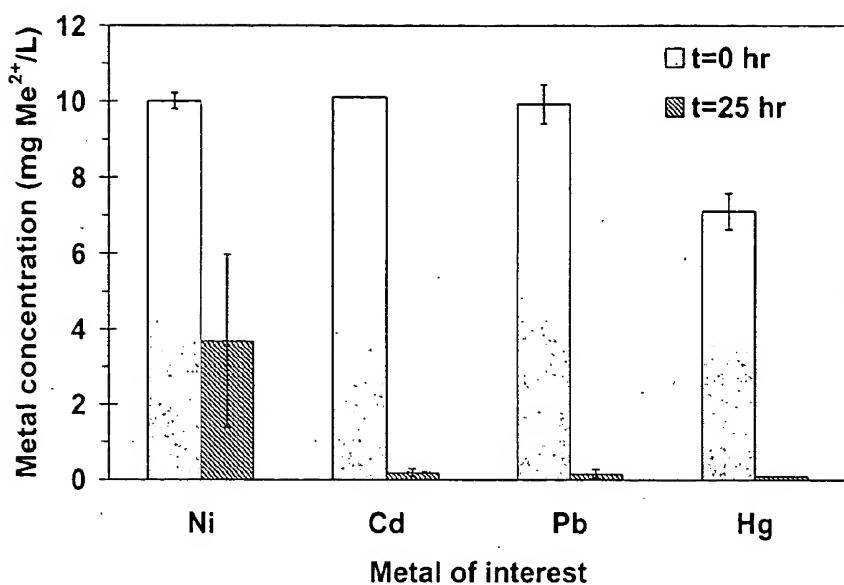


FIG. 7a

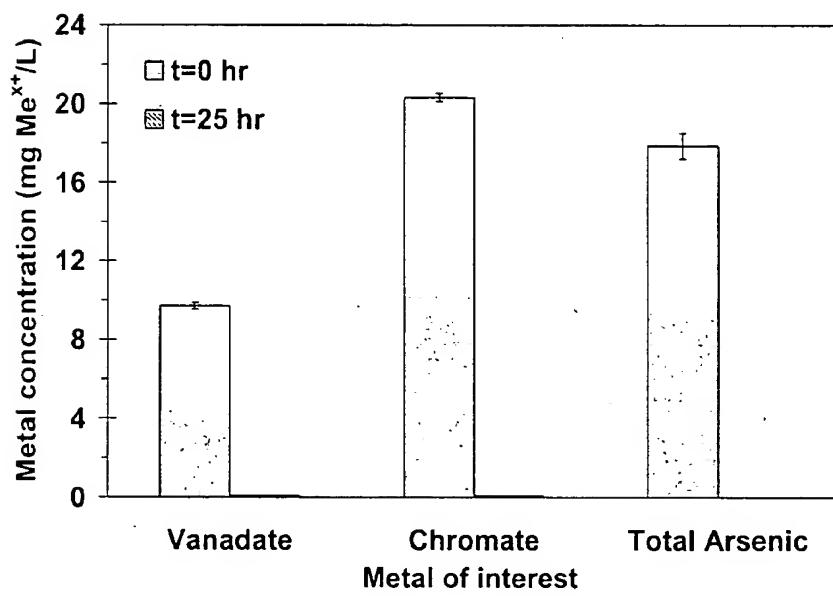


FIG. 7b

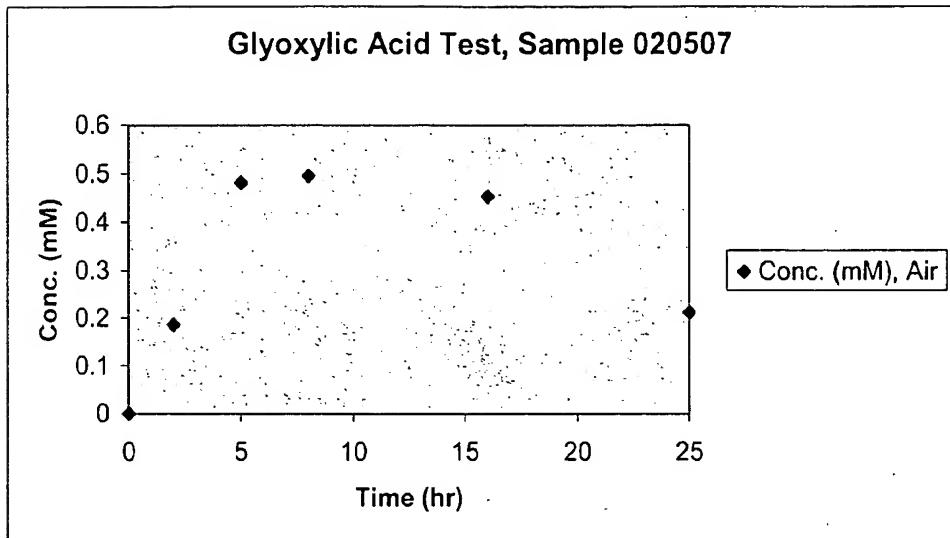


FIG. 8

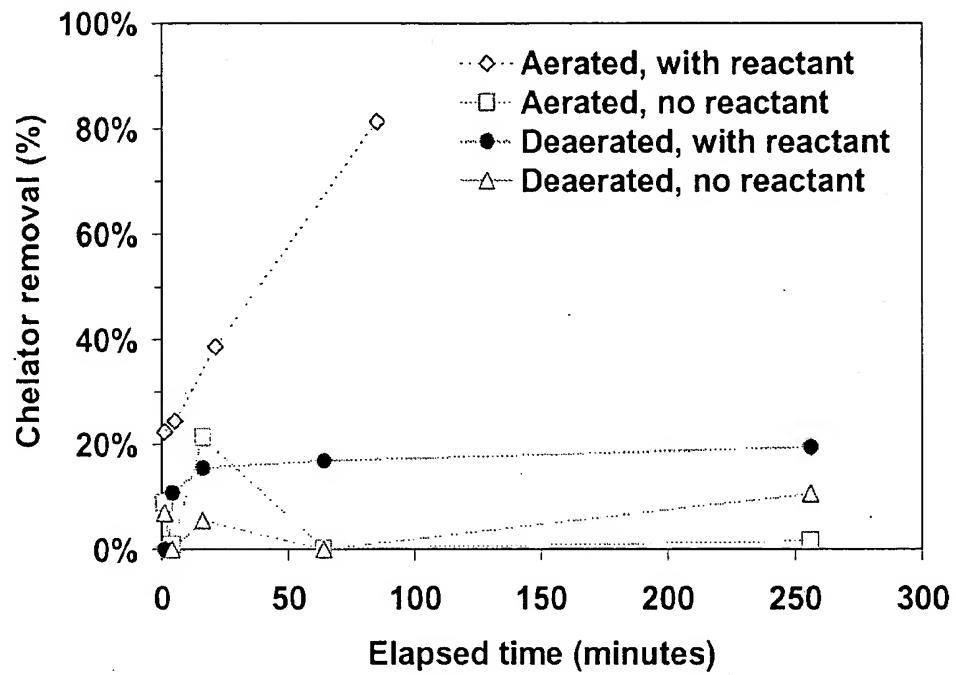


FIG. 9a

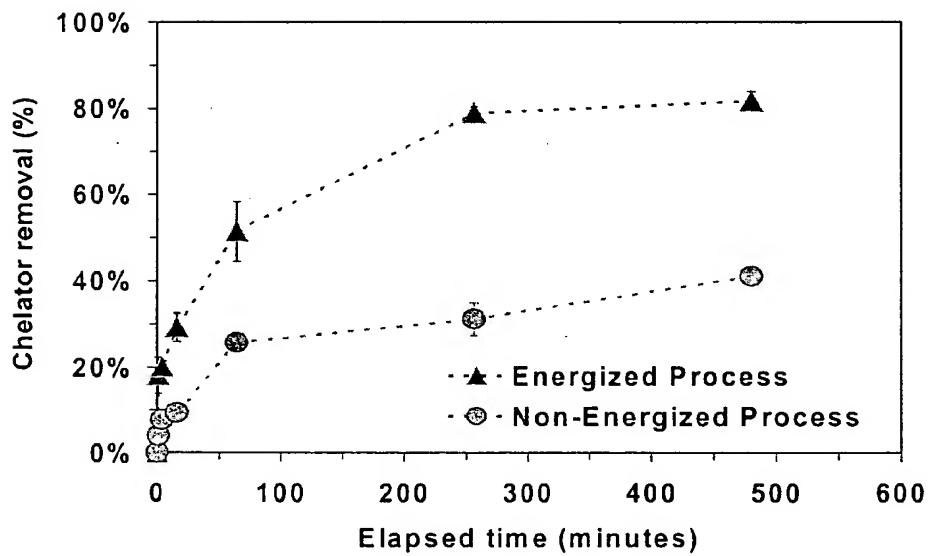


FIG. 9b

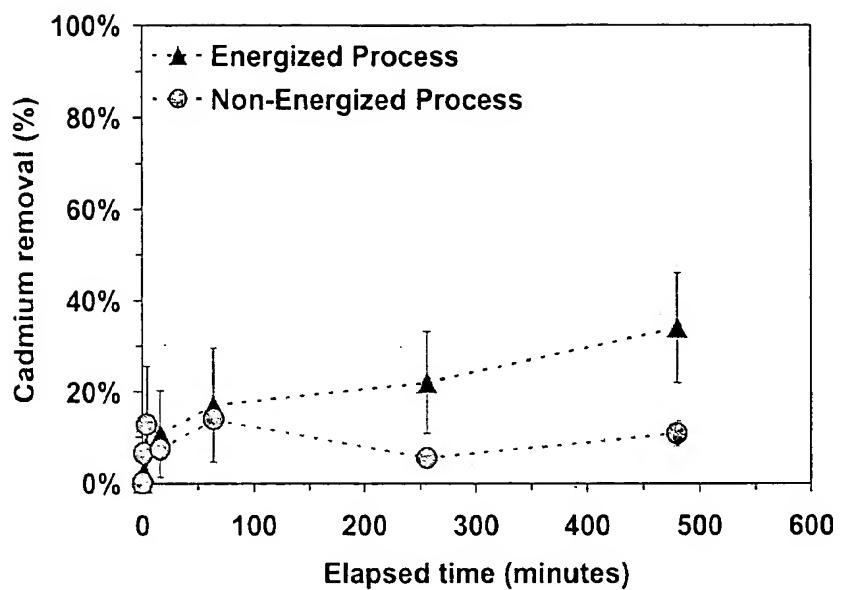


FIG. 10

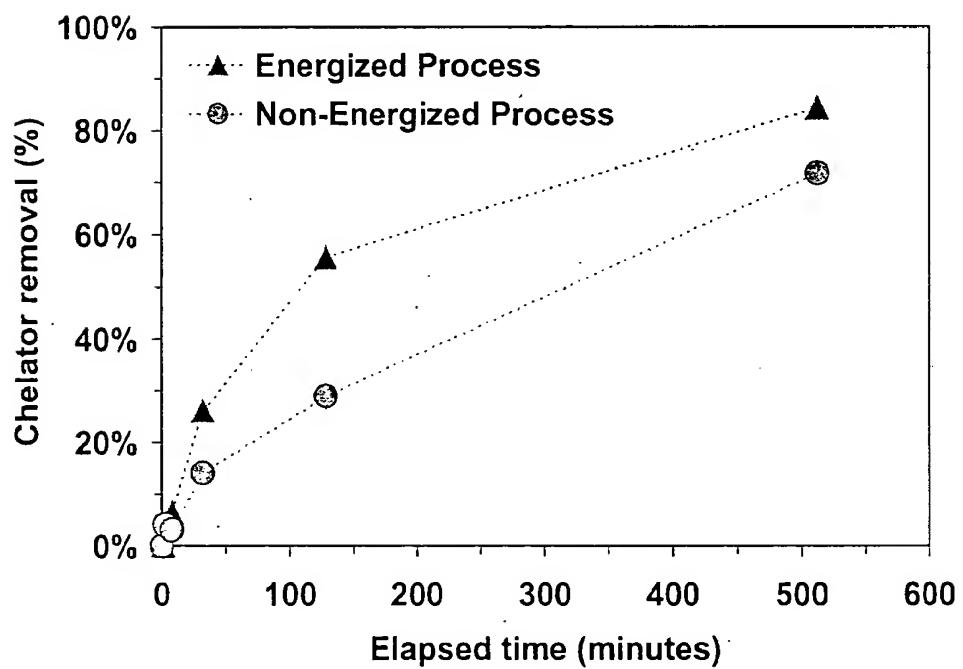


FIG. 11

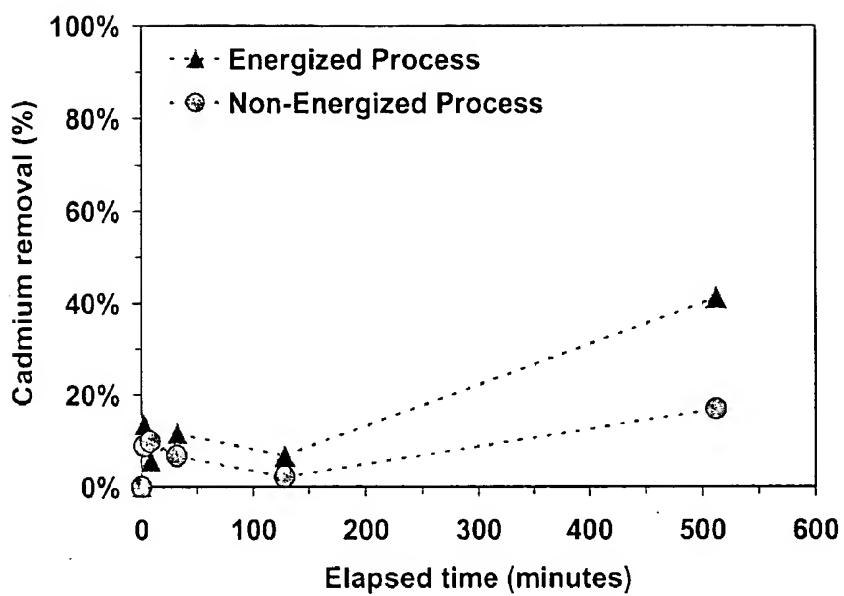


FIG. 12

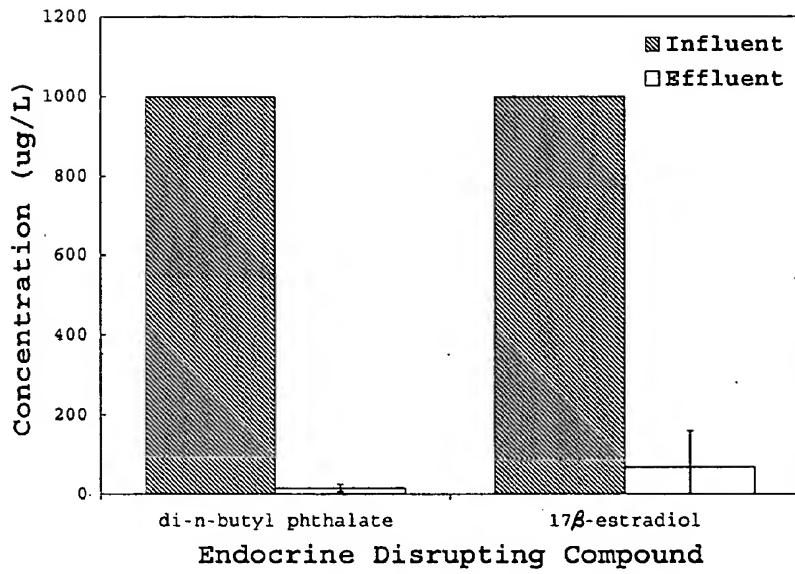


FIG. 13

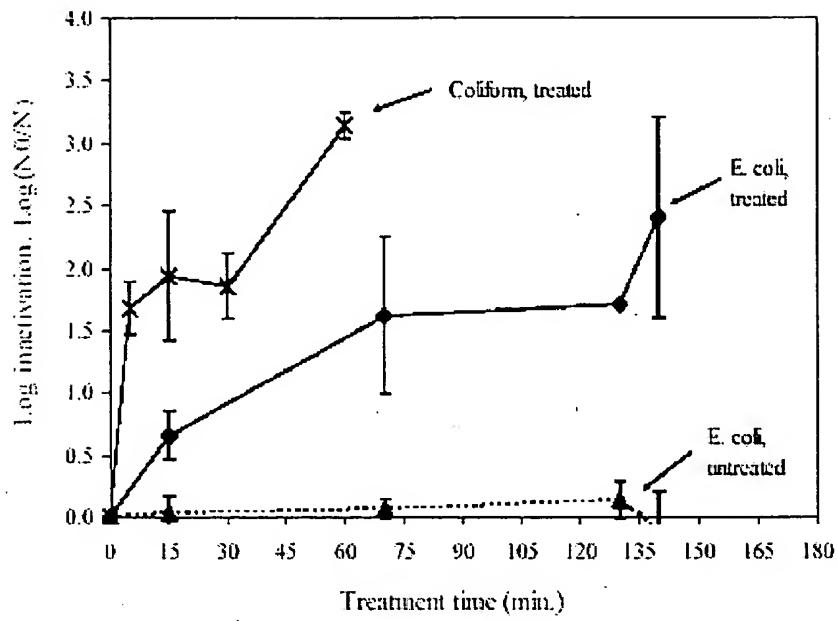


FIG. 14

CLAIMS

We claim:

1. A water treatment method, comprising the steps of:
providing a source of solid-permeable metal arrangement, and
contacting influent water including at least one contaminant with said metal in the presence of an oxygen comprising gas flow, wherein an outlet flow following said contacting step provides at least one of reduction in a concentration of said contaminant in said influent and precipitation or co-precipitation, or reduction to metal form of at least a portion of said contaminant with said metal to form a metal sludge.
2. The method of claim 1, wherein said metal comprises Fe.
3. The method of claim 2, wherein said Fe is contained within a fluidized bed reactor.
4. The method of claim 3, wherein said fluidized bed reactor includes at least one magnetic field source, further comprising the step of magnetic fluidizing.
5. The method of claim 1, further comprising the step of separating said outlet flow into treated effluent and said metal sludge.
6. The method of claim 1, wherein said separating step comprises sedimentation or filtration of said metal sludge.

7. The method of claim 1, wherein at least a portion of said influent water includes a chelated metal, said chelated metal provided by the step of contacting soil or sediment with a chelating agent to form said chelated metal.

8. The method of claim 7, wherein said chelating agent comprises EDTA.

9. The method of claim 1, wherein said contacting step is performed at ambient conditions and exclusive of any externally applied energy sources.

10. The method of claim 1, wherein said oxygen comprising gas is air.

11. The method of claim 1, wherein said metal comprises Fe filings, steel wool or porous Fe comprising granules.

12. A water treatment system, comprising:

a reaction chamber including a solid fluid permeable metal arrangement therein, at least one inlet and at least one outlet, and

a source of an oxygen comprising gas, said oxygen comprising gas fluidically connected to said reaction chamber,

wherein when influent water including at least one contaminant is contacted with said metal in the presence of said oxygen comprising gas, a flow emerging from said outlet provides at least one of reduction in a concentration of said contaminant in said influent and precipitation

or co-precipitation of at least a portion of said contaminant with said metal to form a metal sludge.

13. The system of claim 12, wherein said reaction chamber is a fluidized bed.

14. The system of claim 13, wherein said system includes at least one magnetic field source.

15. The system of claim 12, wherein said metal comprises Fe.